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LOW-TEMPERATURE QUANTUM RELAXATION IN A SYSTEM OF MAGNETIC NANOMOLECULES

N. V. Prokof'ev^{1,3} and P. C. E. Stamp^{2,4}

¹ *Russian Research Center "Kurchatov Institute", 123182 Moscow, Russia*

² *Physics Department and Canadian Institute for Advanced Research, University of British Columbia, 6224 Agricultural Road, Vancouver B.C., V6T 1Z1, Canada*

³ *Laboratoire de Magnétisme Louis Néel, CNRS, BP 166, 38042 Grenoble, Cedex 9, France*

⁴ *Max Planck Institut-LCMI, 25 Avenue des Martyrs, 38042 Grenoble, France*

We argue that to explain recent resonant tunneling experiments on crystals of Mn_{12} and Fe_8 , particularly in the low- T limit, one must invoke *dynamic* nuclear spin and dipolar interactions. We show the low- T , short-time relaxation will then have a $\sqrt{t/\tau}$ form, where τ depends on the nuclear T_2 , on the tunneling matrix element Δ_{10} between the two lowest levels, and on the initial distribution of internal fields in the sample, which depends very strongly on sample shape. The results are directly applicable to the Fe_8 system. We also give some results for the long-time relaxation.

1. Recent experiments on magnetic relaxation of molecular crystals of Mn_{12} and Fe_8 have found strong evidence for quantum tunneling-mediated relaxation at low temperatures [1–7]. This evidence comes from striking resonances observed in the relaxation rate at certain values of applied external magnetic field H (when the energy levels of magnetic states on opposite sides of the potential barrier match each other). These resonances exist both in the low- T limit (when only the two lowest electronic energy levels of each molecule are involved), and also in the thermally activated regime, when tunneling clearly takes place between higher levels. In the Fe_8 system, the low- T relaxation rate peak at $H = 0$ is over 4 orders of magnitude above the rate at $H = 0.1T$, off resonance!

In these systems the anisotropic potential acting on the molecular "giant spins" (of spin quantum number S) is dominated by a strong parabolic easy-axis term, of form $\|\mathcal{H}_2^{(0)}\| = -(\mathcal{D}/S)S_z^2$; tunneling is caused by weak transverse perturbations on this. For Fe_8 , $\mathcal{D} \sim 0.27\text{ K}$, whereas in Mn_{12} , $\mathcal{D} \sim 0.61\text{ K}$; and $S = 10$ for both molecules [1–7]. Here we concentrate on the relaxation at low T (below $T_c \sim 2.2\text{ K}$ and $\sim 0.4\text{ K}$, for Mn_{12} and Fe_8 respectively [8]), near $H = 0$, so that only the two lowest levels $|10\rangle$ and $| - 10\rangle$ of $\|\mathcal{H}_2^{(0)}\|$ are involved - they are coupled by a tunneling matrix element Δ_{10} , which can in principle be calculated [9], but only if all relevant transverse couplings are known [10]. Present estimates range over several orders of magnitude, but it seems unlikely that Δ_{10} exceeds 10^{-8} K for either system - here we will treat it as an independent parameter.

The low- T , low- H limit is particularly interesting be-

cause of the following simple reasoning. Recall first that a standard phase space argument [11] tells us that the phonon-mediated spin relaxation must go like $\tau^{-1} \sim \xi^3[2N(\xi) + 1]$, where $\xi = |\mathcal{E}_S - \mathcal{E}_{-S}|$ is the bias between the two lowest levels in an applied field, and $N(\xi)$ is the Bose function. If we ignore the hyperfine and dipolar fields, $\xi = 2g\mu_B S|H|$, and we get $\tau^{-1} \sim |H|^3$; however it is crucial to understand that even if we include these fields, this will not change the prediction of a minimum in τ^{-1} around $H = 0$, *unless* we include their *dynamics*. This is because the typical bias caused by dipolar fields alone is $\xi_{Dip} \sim 0.1 - 0.5\text{ K}$; with Δ_{10} in the nanokelvin range the effect of a distribution of *static* hyperfine and dipolar fields in the sample will be simply to force almost all molecules off resonance (resonant tunneling requiring that $\xi < \Delta_{10}$, in the low- T limit). The only way then for the molecules to relax is then via spin-phonon interactions, and the effect of the spread in static fields is simply to smear the minimum around $H = 0$. Notice that this argument holds even if the static fields have a transverse component, unless this is $\sim 5T$ (enough to raise Δ_{10} to the experimental resonance linewidth in energy, ie., $\sim 0.1 - 1\text{ K}$ for the Mn_{12} and Fe_8 systems [12]); this enormous value is $\sim 10^2$ times the actual hyperfine/dipolar field combination! Thus the low-field, low- T experiments force us to consider the dynamics of the hyperfine and dipolar fields, which, by varying the bias at each molecular site *in time*, is capable of continually bringing more molecules to resonance.

At first glance, in the low- T limit only the dynamic nuclear fields (ie., hyperfine and nuclear dipolar fields) can then play a role in the relaxation- once $kT \ll \mathcal{D}$, all dipolar flip-flop processes are frozen out [13]. However we shall see that although one needs the rapidly-fluctuating hyperfine field to bring molecules initially into resonance, after this the gradual adjustment of the dipolar fields across the sample, caused by tunneling relaxation, is sufficient to bring a steady further supply of molecules into resonance, and allow continuous relaxation. This process is particularly important in Fe_8 , where the hyperfine couplings are very small. The fluctuating nuclear spin field also makes the tunneling *incoherent*. One can

then write down a *classical* kinetic equation for the magnetisation, whose solution at short time is found below to have a square root behaviour, for almost any sample shape (although the characteristic time in the decay depends strongly on the shape).

We shall thus find that not only do the low-T, low-H experimental results force the inclusion of the *dynamics* of the internal fields into the theory - this dynamics also leads to a characteristic (and experimentally testable) prediction for the form of the relaxation.

2. We will treat the problem using a Hamiltonian

$$H = \frac{1}{2} \sum_{ij} V_{ij}^{(d)} \tau_z^{(i)} \tau_z^{(j)} + \sum_i \Delta_{10} \tau_x^{(i)} + \sum_{ik} V^{(N)}(\tau_z^{(i)}, \vec{I}_k) + H^{NN}, \quad (1)$$

where the first term describes the dipolar-dipolar interactions between molecules, the second describes tunneling, the third couples magnetic molecules to nuclear spins $\{\vec{I}_k\}$, and the last term describes interactions between the nuclear spins. This is an effective Hamiltonian operating in the subspace of the two lowest levels of each molecule; we choose the basis set to be $|S_z = \pm S\rangle$; τ_z and τ_x are Pauli matrices, and $\{i\}$, $\{j\}$ label molecular sites.

We have ignored the transverse part of the dipolar coupling, since it can only renormalise Δ_{10} in an unmeasurable way - all flip-flop transitions to states with $S_z \neq \pm S$ are frozen out at low T . Nuclear spin effects are in principle more subtle - however, since the dipolar fields in (1) are diagonal and not dynamic unless some of the molecules flip, one has only to understand the dynamics of individual molecules, coupled to the nuclear bath, assuming that dipolar fields are frozen. This problem was solved in Ref. [14], sec. 4. If the nuclear T_1 is long (which it will be at these temperatures, since it is driven by dipolar flip-flop processes), then the hyperfine bias field acting on a given molecule rapidly fluctuates at a rate T_2^{-1} , and over an energy scale Γ_2 which is also roughly $\sim T_2^{-1}$. Typically $T_2^{-1} \sim 10^{-7} - 10^{-5} K$, so that we expect $\Delta_{10} \ll T_2^{-1}$. Thus at short times we can write the bias $\xi_j(t)$, at molecular site j , as $\xi_j(t) = \xi_j + \delta\xi_j(t)$, where ξ_j results from the sum of the quasi-static dipolar and hyperfine fields, with only a small rapidly fluctuating component $\delta\xi_j(t)$, which nevertheless sweeps over a bias range much larger than Δ_{10} . One then finds [14] that a molecule in quasi-static bias ξ relaxes *incoherently* at a rate

$$\tau_N^{-1}(\xi) \approx \tau_0^{-1} e^{-|\xi|/\xi_0}. \quad (2)$$

$$\tau_N^{-1}(\xi = 0) \equiv \tau_0^{-1} \approx \frac{2\Delta_{10}^2}{\pi^{1/2}\Gamma_2}. \quad (3)$$

The parameter ξ_0 depends on the average number λ of nuclear spins which co-flip with S . If $\lambda < 1$, then $\xi_0 \sim$

Γ_2 ; in the opposite limit $\xi_0 \sim \lambda|V_{ki}^{(N)}|$. For both Fe_8 and Mn_{12} , $\lambda < 1$ is most likely [15]; in any case, $\xi_0 \ll E_D$, where E_D is the total dipolar coupling from nearest neighbour molecules, and the exact value of ξ_0 will not be too important.

We now define a normalised 1-molecule distribution function $P_\alpha(\xi, \vec{r}; t)$, with $\sum_\alpha \int d\xi \int d\vec{r} P_\alpha(\xi, \vec{r}; t) = 1$. It gives the probability of finding a molecule at position \vec{r} , with polarisation $\alpha = \pm 1$ (ie., in state $|S_z = \pm S\rangle$), having a bias energy ξ , at time t . Molecules having bias energy ξ undergo transitions between $|S_z = S\rangle$ and $|S_z = -S\rangle$ at a rate given by (2). Flipping these molecules then changes the dipolar fields acting on the whole ensemble, bringing more molecules into near (or away from) resonance, and leading to a self-consistent evolution of $P_\alpha(\xi)$ in time. The general solution of this problem requires a kinetic equation for $P_\alpha(\xi, \vec{r}; t)$.

3. To derive a kinetic equation for $P_\alpha(\xi, \vec{r}; t)$, we again assume that dipolar and hyperfine fields are frozen (apart from the nuclear T_2 fluctuations just discussed), *unless* a molecule flips. All kinetics then come from these flips, along with the resulting adjustment of the dipolar field. We may then derive a kinetic equation in the usual way [16], by considering the change in P_α in a time δt , caused by molecular flips, at the rate $\tau_N^{-1}(\xi)$, around the sample. This yields

$$\begin{aligned} \dot{P}_\alpha(\xi, \vec{r}) = & -\tau_N^{-1}(\xi)[P_\alpha(\xi, \vec{r}) - P_{-\alpha}(\xi, \vec{r})] \\ & - \sum_{\alpha'} \int \frac{d\vec{r}'}{\Omega_0} \int \frac{d\xi'}{\tau_N(\xi')} \left[P_{\alpha\alpha'}^{(2)}(\xi, \xi'; \vec{r}, \vec{r}') \right. \\ & \left. - P_{\alpha\alpha'}^{(2)}(\xi - \alpha\alpha' V_D(\vec{r} - \vec{r}'), \xi'; \vec{r}, \vec{r}') \right], \end{aligned} \quad (4)$$

where $P_{\alpha\alpha'}^{(2)}(\xi, \xi'; \vec{r}, \vec{r}'; t)$ is the two-molecule distribution, giving the normalized joint probability of finding a molecule at site \vec{r} , in state $|\alpha\rangle$ and in a bias ξ , whilst another is at \vec{r}' , in state $|\alpha'\rangle$, and in a bias ξ' . $P^{(2)}$ is linked to higher multi-molecule distributions by a BBGKY-like hierarchy of equations [16]. The first term on the right-hand side of (4) describes the local tunneling relaxation, and the second non-local term (analogous to a collision integral) comes from the change in the dipolar field at \vec{r} , caused by a molecular flip at \vec{r}' ; the dipolar interaction $V_D(\vec{r}) = E_D[1 - 3\cos^2\theta]\Omega_0/r^3$, where Ω_0 is the volume of the unit molecular cell, and $\int d\vec{r}'$ integrates over the sample volume.

We will assume that at $t = 0$ the sample is fully polarized; the initial relaxation can then be treated in a dilute solution approximation for the fraction $(1 - M)/2 \ll 1$ of flipped molecules (where $M = \int d\xi \int (d\vec{r}/\Omega_0) [P_+(\xi, \vec{r}) - P_-(\xi, \vec{r})] \equiv \int d\xi \int (d\vec{r}/\Omega_0) M(\xi, \vec{r})$). The bimolecular distribution function $P^{(2)}$ factorizes in this limit, ie., $P^{(2)}(1, 2) = P(1)P(2)$. The simplest case one may study is that of an *ellipsoidal* sample, where the macroscopic

demagnetization field is uniform. The field distribution around randomly placed dipoles is well-known [17] to be a Lorentzian up to a high-energy cutoff defined by E_D

$$P_\alpha(\xi) = \frac{1 + \alpha M(t)}{2} \frac{\Gamma_d(t)/\pi}{[\xi - \alpha E(t)]^2 + \Gamma_d^2(t)} ;$$

$$\Gamma_d(t) = \frac{4\pi^2}{3^{5/2}} E_D (1 - M(t)) ; \quad (5)$$

$$E(t) = c E_D (1 - M(t)) , \quad (6)$$

where c is a sample shape dependent coefficient [18], and $E(t)$ is the time-dependent internal field. Then (4) gives

$$\dot{M}(t) = -M(t) \frac{2}{\tau_0} \int d\xi e^{-|\xi|/\xi_0} \frac{\Gamma_d(t)/\pi}{[\xi - E(t)]^2 + \Gamma_d^2(t)} . \quad (7)$$

At very short times $t < \tau_0 \xi_0 / E_D$ this gives a linear relaxation $M(t) = 1 - 2t/\tau_0$, unobservable because $\xi_0/E_D \ll 1$. For $t \gg \tau_0 \xi_0 / E_D$ one gets

$$\dot{M}(t) = -\frac{1}{2\tau_{short}} \frac{M(t)}{1 - M(t)} ; \quad (8)$$

$$\tau_{short}^{-1} = \frac{\xi_0}{E_D \tau_0} \frac{32\pi}{3^{5/2}(c^2 + 16\pi^2/3^5)} . \quad (9)$$

Since (7) itself is only valid when $1 - M(t) \ll 1$, we simply write

$$M(t) \approx 1 - \sqrt{t/\tau_{short}} ; \quad \left(\frac{E_D}{\xi_0} > \frac{t}{\tau_0} > \frac{\xi_0}{E_D} \right) . \quad (10)$$

The square-root behaviour will be observable experimentally over a wide time range, since $E_D/\xi_0 \gg 1$. Note also that τ_{short} is sample shape dependent even assuming a *homogeneous* demagnetisation field. If the sample is not ellipsoidal, than the above analysis is not correct because the problem becomes essentially inhomogeneous. We then return to the kinetic equation (4), and notice that if the demagnetisation varies on a length scale much greater than the average distance between flipped spins, then (7) is simply modified to

$$\dot{M}(\vec{r}, t) = -M(\vec{r}, t) \frac{2}{\tau_0} \int \frac{d\xi}{\pi} \frac{\Gamma_d(\vec{r}, t) e^{-|\xi|/\xi_0}}{[\xi - E(\vec{r}, t)]^2 + \Gamma_d^2(\vec{r}, t)} . \quad (11)$$

where $\Gamma_d(\vec{r}, t)$ and $E(\vec{r}, t)$ are defined in terms of $M(\vec{r}, t)$ analogously to (5) and (6); the solution is then identical to (10) except that τ_{short} is modified to

$$(\tau_{short}^{(inh)})^{-1} \sim \xi_0 N(0) \tau_{short}^{-1} , \quad (12)$$

where $N(0) = \int d\vec{r} \sum_\alpha P_\alpha(\xi = 0, \vec{r}; t = 0)$ is the *initial* "density of states" for the dipolar field distribution, integrated over the whole sample, at bias $\xi = 0$; typically $N(0) \sim 1/E_{Dm}$, where E_{Dm} is the average demagnetization field.

In order to verify these results, and to see when the square-root behaviour breaks down, we have performed Monte Carlo (MC) simulations of the relaxation for various sample geometries, by the usual procedure - during each time interval $\delta t \ll \tau_0$ one flips molecules with probability $1 - \exp\{-\delta t/\tau_N(\xi)\}$ and then recalculates the dipolar field distribution, now altered by the flipped molecules (cf. Fig.1). The system size we can simulate is not really macroscopic [19], but finite size corrections clearly do not change the two main predictions coming from eqtns (9)-(12), viz., (i) universality of the square-root relaxation at short times and (ii) the characteristic dependence in (12) of the relaxation time on sample geometry. Clearly, the fastest relaxation will be observed in nearly-ellipsoidal samples.

It will thus be very interesting to check in the low-T limit for this square-root relaxation, using *different sample shapes*. Our calculations are most immediately applicable to the Fe₈ system [7], where the field distribution is almost entirely due to dipolar spread [20]. Confirmation of our predictions would then provide strong evidence for the dynamic relaxation mechanism discussed here. We emphasize that at higher T we do *not* expect \sqrt{t} relaxation, since then dipolar flip-flop processes interfere, and T_1 becomes short [21]; moreover, the magnetisation reversal also proceeds via higher levels, through mixed activation/tunneling processes. Coupling to the phonon bath is then crucial, which essentially changes the theory.

Finally, we consider the relaxation when $t \gg \tau_{short}$. This problem is greatly complicated by the development of intermolecular correlations in $P^{(2)}$, $P^{(3)}$, etc., so that one may no longer factorize them. However one way of avoiding this *experimentally* would be to let the system substantially relax at high T, then cool to low T; one would then be in the long-time relaxation regime, but with initial condition arranged to give a factorizable $P^{(2)}$. In this limit another analytic solution for the homogeneous (ie., ellipsoidal) case can be found from (4), when $M \ll 1$ and $P_{\alpha\alpha'}^{(2)}(\xi, \xi'; \vec{r}, \vec{r}') = P_\alpha(\xi)P_{\alpha'}(\xi')$; one finds *exponential* relaxation, at a rate

$$\tau_{long}^{-1} \approx \frac{2\xi_0}{E_{max} \tau_0 [1 + \kappa \ln(E_{max}/\pi \xi_0)]} , \quad (13)$$

where $\kappa \sim 1$ is a numerical coefficient, and E_{max} is the spread in dipolar fields in this nearly depolarized limit. Details of the derivation will be given in a longer paper [22].

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Figure 1: (a) Monte Carlo (MC) simulations of the relaxation in two samples, each made from a cubic lattice

of molecules. In (a) the relaxation is shown as a function of $\sqrt{t/\tau_0}$ for (1) a cubic sample of $(50)^3$ molecules, and (2) for a sphere of diameter 50 lattice spacings ((b) shows the same relaxation as a function of t/τ_0). The dashed line shows \sqrt{t} behaviour; the sample relaxation shows multimolecule correlation effects once $M(t) \lesssim 0.93$.

Figure 2 The density of states $N(\xi)$ for the distribution of bias fields, integrated over the sample (cf. text) is shown for time $t = 0$ (where finite size effects smear the zero energy delta function), and for $t = 0.1\tau_0$, for the spherical sample. Energy (and density of states) use units where $\xi_0 = 1$ and $E_D = 20$. The fraction of states in the resonant window of width ξ_0 around zero energy, at $t = 0$, was 0.79 (sphere), and 0.037 (cube); the ratio $\sqrt{0.79/0.036} \approx 4.6$ corresponds fairly well to the ratio ~ 4 between the straight-line slopes in (a).

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- [7] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, and D. Gatteschi, Phys. Rev. Lett., **78**, 4645 (1997).
- [8] These numbers are taken from the experiments [5,7]; the crossover is clear from the T-independent relaxation rate below T_c .
- [9] See, e.g., L. van Hemmen and A. Suto, Physica B **141**, 37 (1986).
- [10] Note that even very small higher-order transverse couplings (up to the 20th-order in S^+ and S^-) can make important contributions to Δ_{10} , simply because lower-order couplings contribute to Δ_{10} with large exponents (e.g., the transverse coupling ${}^\perp\mathcal{H}_0^{(2)} = E(S_x^2 - S_y^2)$ gives a contribution $\sim E(E/2D)^9$), thereby strongly suppressing their effect on Δ_{10} . This makes Δ_{10} impossible to calculate, since such higher-order couplings are unmeasurable.
- [11] A. Abragam and A. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon (1970).
- [12] Recall that the effect on Δ_{10} from a static transverse H is $\sim g\mu_B SH_\perp (g\mu_B SH_\perp/D)^{19}$, and that for the Mn₁₂ and Fe₈ systems, $(D/g\mu_B S) \sim 10T$.
- [13] The dipolar flip-flop transitions at low T go at a rate $\lambda_{fl} \sim \Omega_{dip} \exp\{-(\mathcal{E}_9 - \mathcal{E}_{10})/k_B T\}$, where $\Omega_{dip} \sim 10^6 - 10^8 \text{ Hz}$. Note that the *direct* effect of flip-flop processes on the kinetic equation is very small (the concentration of molecules in state $|9\rangle$ is $\sim \exp\{-(\mathcal{E}_9 - \mathcal{E}_{10})/k_B T\}$); they are dangerous only because they drive nuclear T_1 processes, which can sweep ξ over a much larger range

than ξ_0 .

- [14] N.V. Prokof'ev, P.C.E. Stamp, J. Low Temp. Phys. **104**, 143 (1996); and see also pp. 347-369 in ref. 1.
- [15] In the simplest case where all nuclear spin effects come via the hyperfine coupling $\sum_k \omega_k \vec{s}_k \cdot \vec{I}_k$, summed over the electronic spins in the molecule, one has $\lambda \sim \sum_k (\omega_k/D)^2 \ll 1$ (cf. ref. [14]), for both the Mn₁₂ and Fe₈ systems. Nuclear dipole-dipole interactions will change this estimate, but not drastically.
- [16] See, eg., N.G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland (1981).
- [17] P.W. Anderson, Phys. Rev. **82**, 342 (1951); A. Abragam, *Principles of Nuclear Magnetism* (O.U.P.), Sec. IV.4, p. 125 (1961).
- [18] The coefficient c is defined by eqtn. 6. For a prolate spheroid, $c = (2\pi/3)[a^4 + a^2 - 3a\sqrt{a^2 - 1} \ln(a + \sqrt{a^2 - 1}) - 2]/(a^2 - 1)^2$, where a is the ratio of the longitudinal axis to its perpendicular; analytic formulas can be found for any ellipsoid [22].
- [19] Even with 10^5 molecules, statistical fluctuations in $P_\alpha(\xi, t)$ inside the small resonance window (width ξ_0) are large if $E_D/\xi_0 \gtrsim 30$ (which correspondingly limits the timescale over which (10) is observed). In real systems E_D/ξ_0 can be very large.
- [20] In Fe₈, the hyperfine field is $\sim 3G$ (due mainly to protons), whereas in Mn₁₂, it is more like 250G; in both systems, $E_D \sim 1000G$. Provided $T_1 \gg \tau_{short}$ (so only T_2 fluctuations matter), the *sqr t t* prediction still holds; however the extra large random hyperfine field in Mn₁₂ means that (12) is no longer precisely obeyed [22].
- [21] When $T_1 \ll$ than the experimental time-scale, and hyperfine fields are larger than intermolecular dipolar fields, one finds exponential relaxation at higher T ; see N.V. Prokof'ev and P.C.E. Stamp, preprint (April 1997).
- [22] N.V. Prokof'ev, P.C.E. Stamp, longer paper in preparation, will discuss the long-time behaviour (including the derivation of (13)), intermolecular correlations, and also the low- T behaviour in large applied fields.





